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# **MEMBRANE REFORMER FOR PROTON EXCHANGE MEMBRANE (PEM) FUEL CELLS: NOVEL APPLICATION OF DEPOSITION PROCESS FOR LOW-COST HYDROGEN SEPARATION**

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## **BACKGROUND OF THE INVENTION**

**[0001]** Field of the Invention

**[0002]** This invention is generally related to providing hydrogen separation membranes coated on porous substrates that are useful in membrane steam reformers and methods for making same. These reformers can be integrated with proton exchange membrane (PEM) fuel cells to form power systems

## **SUMMARY OF THE INVENTION**

**[0003]** It is one object of the present invention to overcome the problems and disadvantages of the prior art by providing for novel application/deposition processes for providing hydrogen separation membranes that had been previously cost-prohibitive and displayed poor or inadequate hydrogen transport (permeation rates).

**[0004]** It is still a further object to provide for hydrogen separation membranes having desirable lifetime and stability characteristics, provided by and in accordance with the teachings of the present invention.

**[0005]** It is still a further object of the present invention to provide for improved hydrogen production from light hydrocarbons, such as propane and/or methane, utilizing the exemplary membrane reformer being provided according to the teachings of the present invention. Sulfur-free heavy hydrocarbons (gasoline, kerosene, diesel), oxygenates such as, but not limited to, ethanol, methanol, soydiesel and ammonia may

also be utilized for hydrogen production in accordance with the teachings of the present invention.

**[0006]** Another object is the scaling up of the disclosed membrane surface area and/or the integration into a membrane reformer having mesochannels.

**[0007]** Other objects of the present invention will be apparent to those of ordinary skill in the art.

#### **DETAILED DESCRIPTION OF THE INVENTION**

**[0008]** In the exhibit attached, descriptions of exemplary embodiments of the invention are provided and reference made to the accompanying figures which form the part thereof, and in which are shown by way of illustration of specific embodiments in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural and functional changes may be made without departing from the scope of the present invention.

**[0009]** The foregoing is a description of the preferred embodiments of the invention and has been presented for the purpose of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in the light of the above teaching.

#### **[0010] EXHIBITS**

**[0011]** Exhibit 1 is an exemplary outline/report outlining and detailing the deposition formation of useful membranes in accordance with the teachings of the present invention.

**[0012]** We claim:

**[0013]** 1. A membrane reformer comprising:

**[0014]** a thin leak-tight coating, wherein said thin leak-tight coating transports hydrogen.

**[0015]** 2. The reformer of claim 1, wherein said thin leak-tight coating is comprised of at least one of Pd, Pd alloys and Pd/Ag.

**[0016]** 3. A reformer having a thin leak-tight coating wherein said thin leak-tight coating is formed on a porous substrates, more preferably porous metal substrates.

**[0017]** 4. A reformer having a thin leak-tight coating wherein said thin leak-tight coating is formed on a porous metal substrate that has been polished.

**[0018]** 5. A reformer having a thin leak-tight coating wherein said thin leak-tight coating is formed on a porous metal substrate that has been polished and is treated to contain a diffusion barrier prior to Pd/Ag deposition

**[0019]** 6. A reformer having a thin leak-tight coating wherein said thin leak-tight coating is formed on a porous metal substrate that has been polished and is treated to contain a diffusion barrier and is etched with nitric acid for a short period prior to Pd/Ag deposition

**[0020]** 7. A reformer having a thin leak-tight coating, wherein said thin leak-tight coating transports hydrogen and is provided by a laser direct-write process.

**[0021]** 8. The reformer of claim 3, wherein said laser direct-write process utilizes a Pd/Ag ink with optimum viscosity and minimal organics (solvents, dispersing agents, stabilizers etc ) comprising said ink.

## **Exhibit 1**

### **Part 1. Results of the Phase I Project**

#### **1.0. Summary of the Phase I Project**

Major accomplishments during the Phase I are summarized below, and are presented here at the outset for convenience:

- (1) Thin Pd/Ag membranes of thickness in the about 5 to 10 micron range can be deposited on porous metal substrates using a direct-write process, which is manufacturable and lends itself well to high volume production. The laser direct-write approach offers uniform edge-to-edge deposition, with excellent thickness control in the about 2-10 micron range. The coatings were in good contact with underlying porous metal support as no adherence (or flaking) problems were noticed.

EV 311270660 US

- (2) The thin membranes were found to be leak-tight (nitrogen permeance less than  $0.5\text{e-}9 \text{ m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ ) when tested at room temperature and up to 70 psig pressure.
- (3) A spin-coating method (another coating method that was evaluated) provided acceptable control over thickness, but was less uniform.
- (4) To date, the deposited membranes are not very permeable to hydrogen permeation (permeation is below the resolution of our apparatus) when exposed to 75H<sub>2</sub>/25N<sub>2</sub> gas mixture at temperatures of up to 600 °C and pressures of up to 80 psig. A number of synthetic approaches and alternatives were screened regarding H<sub>2</sub> permeation flux and selectivity, most promising ones identified as well as critical issues and strategies.
- (5) Among the porous metal supports evaluated, an ion-beam treated (polished) Mott support offered the best surface for deposition of uniform thin films. This treatment is also manufacturable and lends itself well to high volume production.

Using XPS and XRD characterization of the Pd/Ag coating, it was determined that the surface of the membrane is deplete in Pd, as the surface composition was 34% Pd-66%Ag (a 70Pd/30Ag ink was used for coating).<sup>1</sup> The absence of hydrogen permeation can be directly attributed to the low surface Pd concentration, but other contamination (elements O, C, Fe, Cr; details in section 1.6 and 2.1) may also be a contributing factor.

The presence of carbon requires modification of the thermal processing (organic bake out and sintering) procedures. It is possible that by thermal processing (between coatings) in air at low temperatures (<350 °C), organics can be totally removed without oxidizing the Pd/Ag coating. Soak temperatures would likely be in the vicinity of 350 C. This low temperature will also not sinter the metal layer or the support significantly. After multiple deposition cycles, single step sintering of the membrane layer should then be attempted, exploring higher soak temperatures, and employing faster ramp rates (the exception being a possible soak for organic removal). Such steps are to be further investigated during the Phase II period.

### **1.1. MesoFuel's Approach**

Our approach involves the deposition of a thin (< 10 microns thick) Pd/Ag coating on porous metal substrates using a low cost and manufacturable laser direct-write process. Additional details on the Pd/Ag ink, metal substrates, and coating process, and performance of the coatings are provided below.

### **1.2. Pd and Pd Alloys**

Pd metal and many of its alloys are well known for their ability to dissociate and diffuse hydrogen. For Pd metal itself, the diffusion of hydrogen and the kinetics of surface processes have been widely studied and modeled [1]. A variety of alloys also have high permeability to hydrogen, and alloys typically have superior mechanical properties [2-3]. In particular, some alloys alleviate the  $\alpha$ - $\beta$  phase transformation that leads to structural distortion and embrittlement. Alloys of Pd and Ag have been the most widely studied, largely because they form a solid solution over the entire composition range, and exhibit a maximum in hydrogen permeability at compositions near 75% Pd/25% Ag [2-4].<sup>1</sup>

During the Phase I period, Pd/Ag powders by an aerosol decomposition process were prepared[5]. (*Sections 3.1 and 4.2.1 in Phase I report*). The exemplary compositions employed were as follows: Aerosol-Derived Powder ink composition: 25 wt% Pd/Ag powder: 75 wt%  $\alpha$ -terpineol [6,7]. The powder was an alloy with composition 75 at %Pd/25 at% Ag. While the desired sub-micron sized particles were obtained using this method (mean diameter 0.7-0.8 microns, *Fig 4.4, Phase I report*), the process was laborious, and resulted in low powder yields.

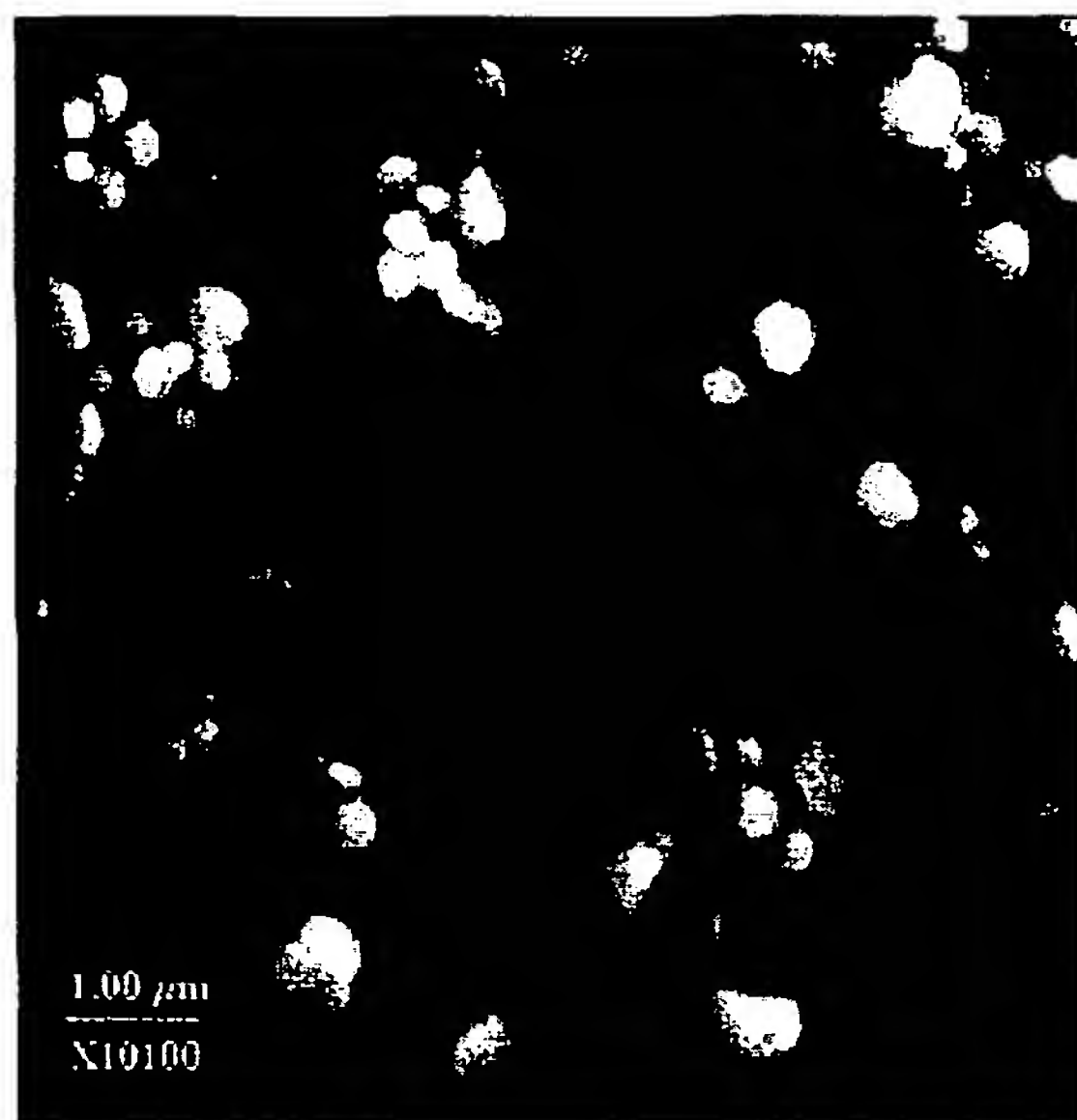
Alternate Pd/Ag ink sources were investigated and identified MRA Laboratories (MRA) (Adams, MA) was identified as a potential source. Subsequently, 70Pd/30Ag (alloy) particles were received in an organic vehicle for evaluation. The as-received ink contained 49.4 wt.-% powder (metal). A composition of 70Pd/30Ag was used for the commercial inks due to the more ready availability of that composition. The literature indicates that the permeability for the 70/30 composition may be approximately 30% of that for the 75/25 composition [2], although Holleck's data indicate a less strong

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<sup>1</sup> A recent (post-Phase I report) EPMA analysis of a different sample showed the surface Pd concentration to be 63% (please see Section 2.1 for more details).

EV 311270660 US

composition dependence [4]. Figure 1.1 shows an SEM micrograph of particles from the ink, indicating spherical as well as disc-shaped submicron particles of relatively narrow distribution. The particles appeared to be relatively similar to the aerosol-derived powder (*Figure 4.4 in Phase I report*). For Pd/Ag membrane deposition during the Phase II period, we will use Pd/Ag inks with Pd contents in the 75-77% range supplied by MRA.



**Figure 1.1.** SEM of particles from the commercial Pd/Ag (70/30) ink obtained from MRA Laboratories, Inc.

### **1.3. Porous Metal Supports**

Porous stainless steel supports, 0.75 inch in O.D., (0.2 micron filter grade) were obtained from Mott Porous Metals. Pd/Ag membranes were deposited on the “as-is” supports as well as on polished supports. Polishing was accomplished by subjecting the supports to ion-beam surface treatment<sup>2</sup>, a low-cost technique that lends itself well to scale-up and manufacturability. Ion beam treatment was done at QM Technologies (QMT) (Albuquerque, NM). This pre-treatment was attempted as an alternative to mechanical steps such as shot-peening, to polish the surface of porous metal substrates. During ion beam treatment, a high energy, pulsed ion beam (hydrogen ions) impinges on the surface for a short period (typically 150 ns), and rapidly melts the

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<sup>2</sup> Mesofuel patent pending



surface of the substrate to a depth of only a few microns. On turning off the ion-beam, the melted top layer is rapidly cooled, and as a result, the bulk properties of the substrate remain unchanged. Although surface porosity was somewhat reduced, the substrates were considerably porous as confirmed by room temperature nitrogen permeation tests. Among the porous metal supports that were evaluated (*Section 2.3, Phase I report*), the ion-beam treated (polished) Mott support offered the best surface for deposition of uniform thin films. This treatment is also manufacturable and lends itself well to high volume production.

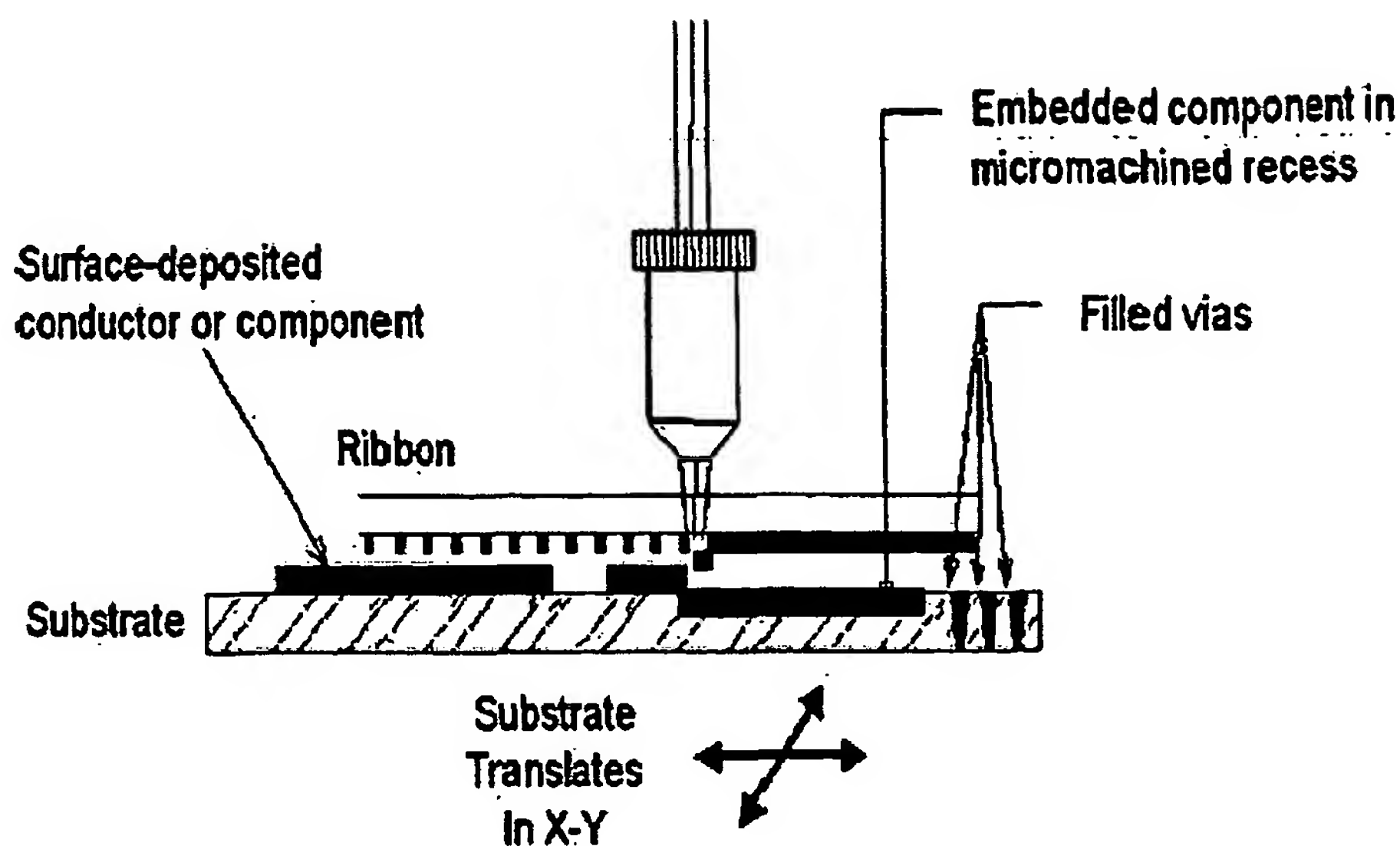
#### **1.4. Direct-Write Deposition**

Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a laser deposition technique that was recently developed by Potomac Photonics, Inc. (PPI) (Lanham, MD). The organic molecules to be deposited are first dissolved in a solvent matrix material to form a dilute solution. When the low fluence short pulse UV laser strikes the target, it warms and vaporizes the solvent locally and releases the organic molecules. MAPLE is an energetically soft process, which can deposit a wide range of materials (such as metal, polymer, and ceramic) onto polymeric, metallic, and ceramic substrates. MAPLE Direct-Write (MAPLE-DW) combines the advantages of Laser Induced Forward Transfer (LIFT) and MAPLE to produce a novel laser-driven process to Direct-Write patterns.

A typical MAPLE Direct-Write system is shown in Figure 1.2. The dilute solution is dispersed onto the optically transparent backing to form a thin film. The result is a "ribbon", which is analogous to a typewriter ribbon. A shaped laser beam strikes the coating from the back through the transparent backing and causes rapid evaporation of the liquid at the ribbon interface, which propels the material towards the receiving substrate. The ribbon is placed in close proximity (25 to 100  $\mu\text{m}$ ) and parallel to the receiving substrate. Patterning, if desired, can be achieved by moving the substrate, scanning the laser beam, or the combination of both. Thickness could be built up by successive depositions. Another advantage of the MAPLE-DW is that it combines both additive and subtractive capabilities. Once the ribbon is removed, the laser used to transfer the matrix material can also be used for patterning the materials deposited, as well as other tasks like micromachining traces and vias, dicing circuits, and trimming



EV 311270660 US  
circuit components.



**Figure 1.2.** Schematic Diagram of Laser Induced Direct-Write Process (PPI).

Further details on the Laser Direct-Write procedure can be found in *Section 3.3.1* of our Phase I report.

### 1.5. Thermal Processing of Pd Alloys

During the thermal processing (e.g. sintering, organics bake out, or elevated temperature hydrogen permeation measurement) of Pd alloys, care must be taken with respect to exposure of the metal to  $H_2$  or  $O_2$  at elevated temperature. Pd-based alloys should not be exposed to  $H_2$  at temperature below approximately 300 °C to avoid the catastrophic  $\alpha$ - $\beta$  phase transformation [2,3,8]. This temperature limit is lowered (<300 °C) for many alloys; the use of Pd alloys (instead of pure Pd) is therefore beneficial for practical applications.

The issues with oxygen exposure relate to the temperature/oxygen partial pressure conditions where PdO forms, and the substantial lattice expansion associated with oxide formation. Oxidation followed by reduction is known to leave residual voids in the Pd. Metallic Pd begins to oxidize to PdO in air at approximately 200 °C, with oxidation becoming essentially complete between about 400 and 500 °C [9]. PdO then decomposes back to metallic Pd in air at approximately 850-900 °C [9,10]. This temperature is lowered roughly 20-30 °C for 30% Ag in Pd [9]. The “window” for PdO

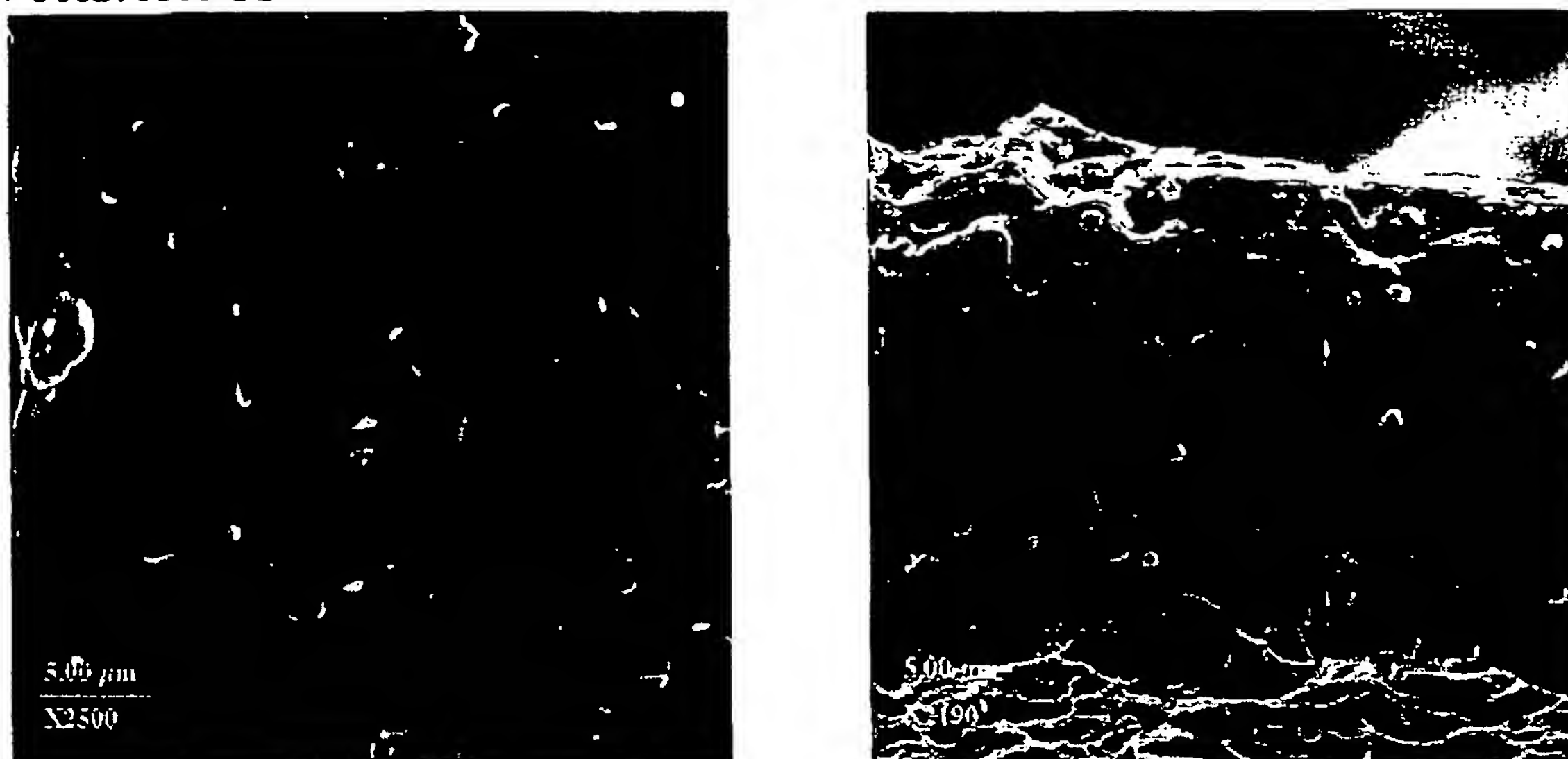
EV 311270660 US

formation and decomposition is also a function of the  $O_2$  partial pressure ( $P_{O_2}$ ). Less detailed information is available for atmospheres other than air; however, the temperature of PdO decomposition (more accurately, Pd-PdO equilibrium temperature) has been measured as a function of  $P_{O_2}$  [10]. For air, this equilibrium temperature is approximately 800 °C; for  $P_{O_2}=10^2$  atm (as found in a normal cylinder  $N_2$ ) it is about 690 °C; and for  $P_{O_2}=10^5$  atm (typical UHP  $N_2$ , it is about 500 °C) [10]. In Pd membrane processing, it is preferable to minimize exposure to even low  $P_{O_2}$  within the temperature window of oxide formation, although brief oxidation has been reported to activate Pd membranes for  $H_2$  permeation, presumably by removal of surface contaminants.

### **1.6. Pd/Ag Membrane Deposition on Polished Porous Stainless Steel**

During the Phase I period, other techniques such as spin-coating, doctor blading (surrogate for tape casting) and centrifugal deposition in addition to the laser direct-write process were evaluated. Details are provided in Sections 4.3.1 to 4.3.3 in the Phase I report, and as reported, spin-coating was found to be promising (in addition to direct-write) and was evaluated in some depth. The supports were treated by an oxidation treatment (following the procedure of Ma [11]) prior to coating to provide a diffusion barrier between the support and the Pd/Ag coating.

SEM micrographs of the Pd/Ag coating on ion beam treated (polished) stainless steel supports are shown in Figure 1.3. (During Phase I, we were able to establish that this polishing step was a crucial pretreatment step for achieving leak-tight Pd/Ag coatings on porous stainless steel; details are provided in *Section 4.1 to 4.3 of the Phase I report*).

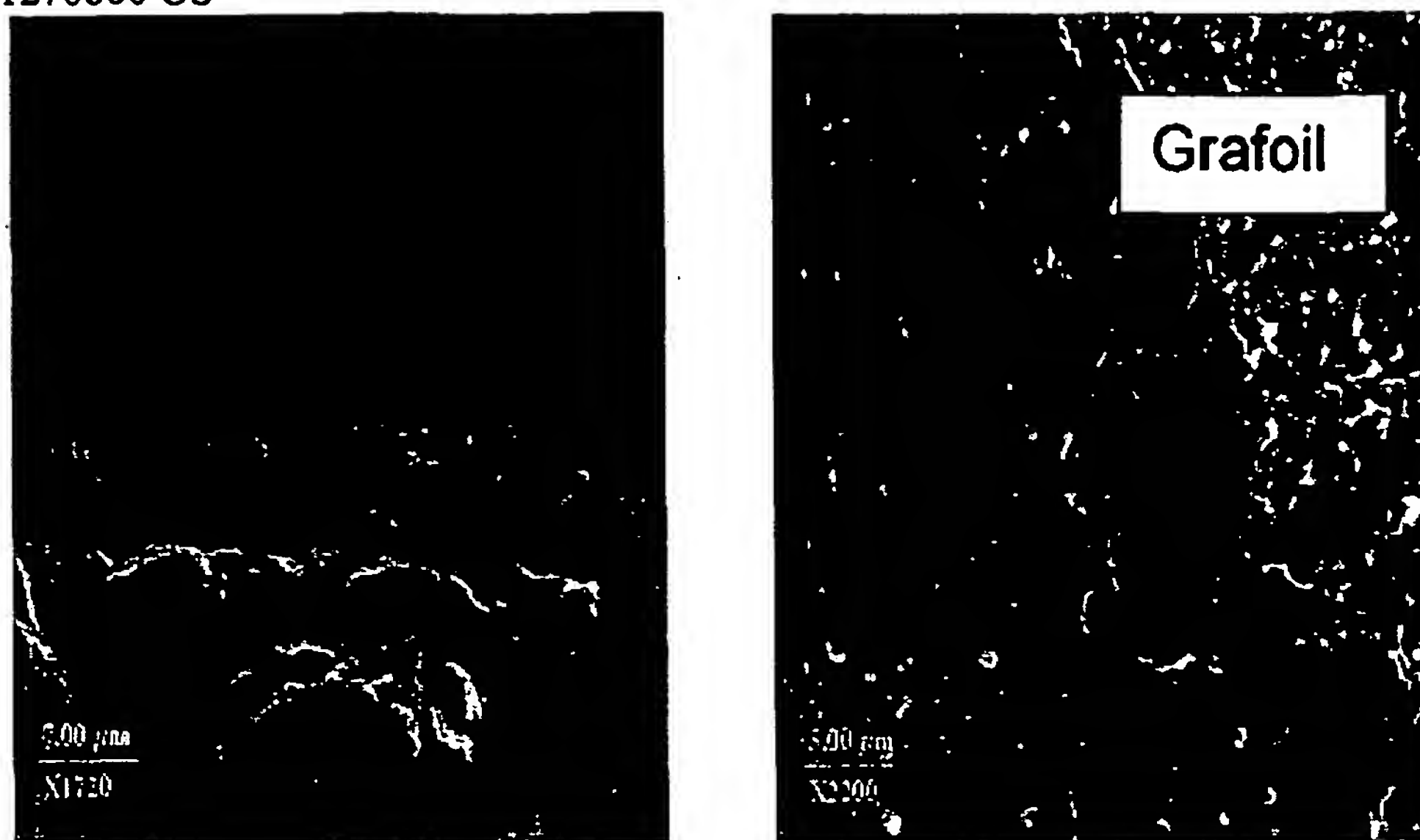


**Figure 1.3.** SEM micrographs showing plan and cross-sectional views of Pd/Ag membrane deposited by spin coating onto ion beam treated stainless steel supports (seven deposition and sintering cycles; *Table 3.1, Phase I report*) (Sample IO-IM).

The Pd/Ag membrane in Figure 1.3 (*Figure 4.11 in the Phase I report*) is approximately 15 microns in thickness, and appeared to be dense and defect free by SEM analysis. The leak-free nature of the membrane was also confirmed by nitrogen leak measurements at room temperature as the measured permeance was less than  $1.e-11 \text{ m}^3/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$  at a differential pressure of about 28 psia. Hydrogen purity levels of 99.99% can be achieved using these leakage rates (as discussed in *Section 4.4 of the Phase I report*). During the multiple coating/sintering cycles required to achieve a leak tight coating (7- cycles in the case of sample 10-IM shown in Figure 1.3), the porous stainless steel metal support itself underwent some undesirable sintering (support polishing characterization is discussed in *Section 4.1 in the Phase I report*).

While coating with the direct-write process on the ion-beam treated (polished) stainless steel supports, however, we were able to achieve a leak-tight coating with only 3-cycles, with the thickness of the coating being 5-6 microns. SEM micrographs of a direct-write coated sample are shown in Figure 1.4 (*Figure 4.19 in the Phase I report*).





**Figure 1.4.** Cross-sectional and plan view SEMs of membrane deposited by LDW (three coats with 850°C N<sub>2</sub> sinter in between each coating) on ion-milled support, followed by final sinter at 900 °C in UHP N<sub>2</sub> (sample P5). Images taken after H<sub>2</sub> permeation testing at MFI.

This sample was also leak-tight, despite the somewhat microporous structure seen in the cross-section. One likely explanation for such a microstructure and the extensive voids is that oxide formation may have occurred, introducing swelling due to the lattice expansion accompanying oxidation. Upon reduction, residual voids may have been left behind that were not sintered out. It is also possible that insufficient time was provided at the proper temperatures to ensure complete organic evolution from the film during the sintering ramp up. (Note: Grafoil gaskets were used to seal the sample in the permeation apparatus and is referenced in Figure 1.4).

Prior to laser direct-write coating, the polished porous metal samples were etched by dipping in concentrated nitric acid for 15 to 120 seconds to provide some minimal surface roughness. This etching promoted adherence of the coating to the substrate and prevented flaking of coating upon sintering.

When subjected to hydrogen permeation tests at 600 °C and 70 psig using a 75%H<sub>2</sub>/25% N<sub>2</sub> gas mixture as the feed, the samples were found to be not permeable to hydrogen. Sample P5 (Figure 1.4) was then subjected to XPS analysis to determine possible reasons for this unexpected behavior of the Pd/Ag coating. A summary of our

EV 311270660 US  
findings is as follows:

- (1) There was no evidence of contamination by iron and any other component from the stainless steel substrate. This is a very positive result because significant inter-metallic diffusion between the stainless steel support and the Pd/Ag coating can drastically reduce hydrogen permeation. As mentioned earlier, prior to coating, the supports were treated at 900 °C in air to form an oxide layer to serve as a barrier against intermetallic diffusion, and this technique appears to have been highly successful.
- (2) Carbon (due to incomplete burnout of organics in the paste or from the Grafoil gasket used for sealing the sample in the hydrogen permeation set-up) was mostly present to the top 1 nm or so (typical for surface contamination). Carbon contamination can reduce hydrogen permeation rates, but it is not expected to cause total stoppage of hydrogen permeation. In fact, one would expect that surface carbon would gasify to methane at 550 to 600 °C when exposed to hydrogen. Sample P5 was exposed to 75% H<sub>2</sub>/25% N<sub>2</sub> for about 15 hours under permeation conditions.
- (3) The outer layer had significant amounts of metal (Pd, Ag) oxides, which may have formed during the sintering stages. Also, during the permeation test, the sample was exposed to a 62% air-38% H<sub>2</sub> gas mixture for about 30 minutes, as an attempt to burn out any carbon *in situ*. The sample was then exposed to 75%H<sub>2</sub>-25%N<sub>2</sub> gas mixture at 600 °C for about 12 h. The presence of surface oxides may be attributed to this treatment also, although one can expect reduction of the oxides during the lengthy exposure to hydrogen.
- (4) The metal composition at the surface was found to be 66% Ag and 34 %PdI, which was an unexpected result. XRD analysis of a different sample that was subjected to 7-deposition-sintering cycles in nitrogen at 900 °C showed that the coating (pre-alloyed, obtained from MRA Lab) was indeed close to 70Pd/30Ag in composition. In fact the calculated unit cell parameter was 3.93 Å, which indicates a composition of 75% Pd/25%Ag according to Wang and Huebner [10]. While migration of Pd and Ag in electroless coated

EV 311270660 US

samples (sequential coating) has been reported to be a function of annealing temperature, the interaction between hydrogen and palladium should support the segregation of palladium towards to the surface [12]. Here, the surface concentration of Pd is lower than that of the bulk concentration.

Other reports indicate slight segregation of silver to the surface under elevated temperature treatments, pointing out to the fact that the elements of lower surface energy tend to segregate towards the surface. The sintering protocol (temperature, gas atmosphere) may need to be carefully optimized to alleviate this problem. As mentioned above, the presence of hydrogen should favor the segregation of Pd towards the surface and should also prevent the formation of oxides.

In conclusion, deposition of thin (< 10 micron thick) Pd/Ag membranes on porous stainless steel using a novel laser direct-write technique that lends itself well to manufacturability has been achieved. Also demonstrated is the fact that polishing substrates using a pulsed ion-beam treatment (polishing) is necessary to obtain a leak-tight coating. This technique is also amenable to scale-up and manufacturability. The membranes were however found to be not very permeable (below the resolution of our apparatus) to hydrogen.

## **Part 2. Phase II Technical Objectives, Approach and Work Plan**

### **2.0. Technical Objective**

We present a 4-fold objective for this Phase II period of the contract, namely:

- (1) Demonstrate hydrogen permeation through direct-write coated membranes
- (2) Demonstrate lifetime and stability to thermal cycling
- (3) Scale-up of membrane surface area by 40X and integration into a MesoChannel™ Membrane Reformer
- (4) Demonstrate pure hydrogen production from light hydrocarbons such as propane using our membrane reformer to improve performance over commercially available 25 micron thick Pd/Ag foils

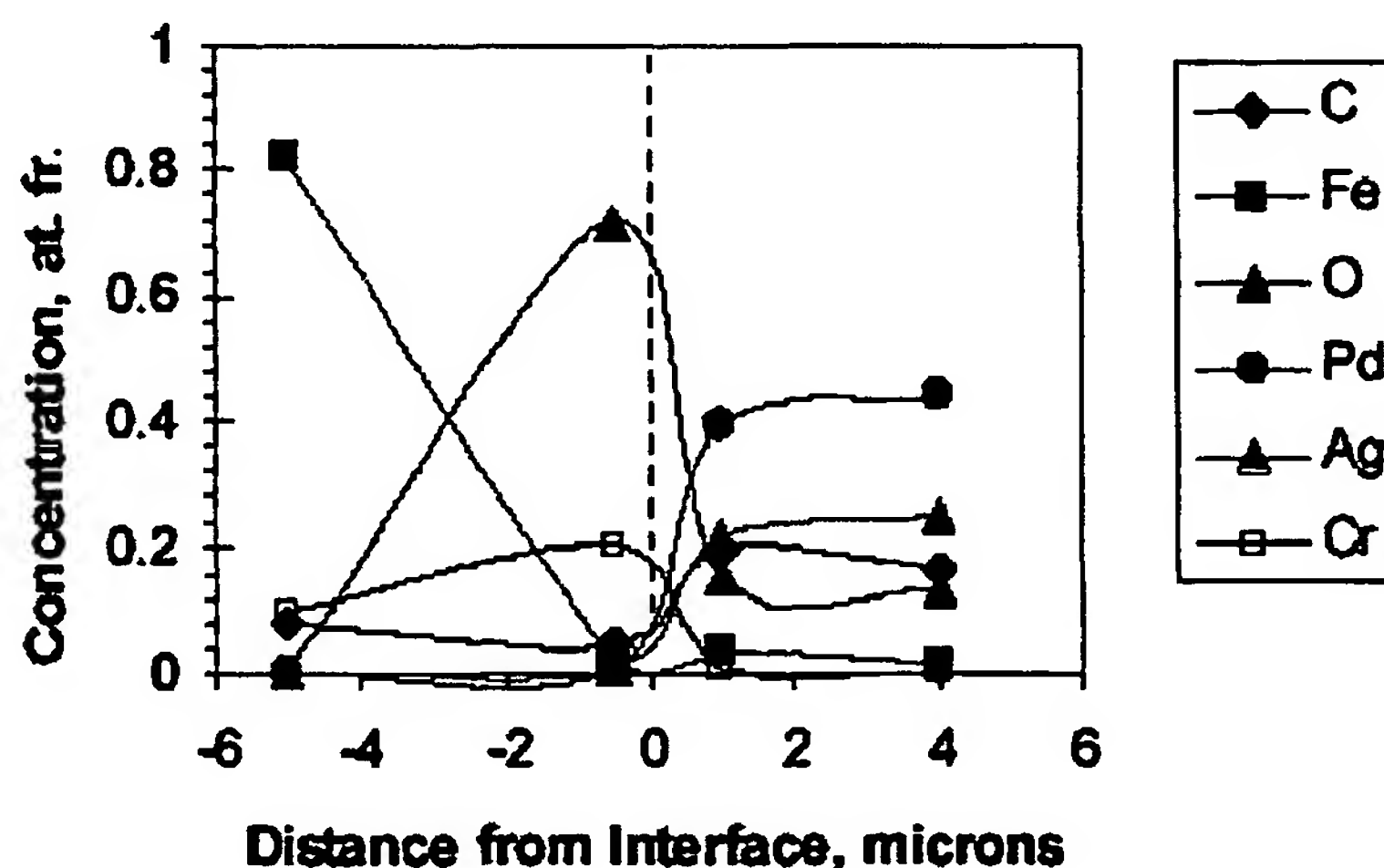
Details are provided below, but first, a brief description of post-Phase I efforts is discussed in Section 2.1 below.



## 2.1. Post-Phase I Efforts

A coated sample labeled as Sample 1 (*Section 4.3.1 in the Phase I report*), was subjected to electron probe microanalysis to obtain depth profile information on the composition of the coating (and to corroborate our XPS results). Figure 1.5 shows a summary of the depth profile and additional observations are as follows:

- (1) The Pd/Ag ratio was found to be 1.7:1 (63 at% Pd) with very slight enrichment of Pd towards the surface and Ag towards the stainless steel substrate. Note: XPS measurements of a different showed that the surface contained only 34% Pd.
- (2) Substantial levels of oxygen and carbon were somewhat uniformly distributed throughout the coating. Atomic ratios: C/(Pd+Ag) was about 0.25 and O/(Pd+Ag) was around 0.25. Since Sample 1 was not subjected to hydrogen permeation (and is not subjected to carbon contamination from Grafoil gaskets; in contrast to Sample P5 that was subjected to XPS analysis), the carbon seen here is from improper burn-out of the organics. These results indicate that we need to pay closer attention to our organic burn-out and sintering protocols, to be addressed during our Phase II effort.



**Figure 1.5.** EPMA depth profile of the Pd/Ag coating on Sample 1 from a 4-spot analyses (5 to 10 micronthick coating, 7-coating cycles). Depth values: Negative: porous SS substrate; zero: interface; positive: Pd/Ag coating. Lines connecting the data points are shown to serve only as a guide to the eye.

- (3) A surface layer of chromium oxide was found beneath the Pd/Ag coating. As discussed in *Section 4.1 of the Phase I report*, we subjected all of our supports to an oxidation treatment at 900 °C to provide a diffusion barrier between the substrate and the Pd/Ag coating.
- (4) Elements Fe and Cr were present in the coating with an average Fe/(Pd+Ag) ratio of 0.05 (atomic) and Cr/(Pd+Ag) ratio of 0.03. Although some diffusion from the support material did occur, overall the oxidation pretreatment step appears to have resulted in an effective diffusion barrier. Porous substrates of high temperature alloys such as Inconel and Hastelloy (Mott Corporation, can provide these materials) may also provide useful substrates.

In summary, depositing of a leak-tight and thin Pd/Ag coating using a novel direct-write method has been achieved and by utilizing pre-treatment protocols, these coatings would be permeable to hydrogen, with permeation rates far exceeding that which is possible with the commercially available 25 micron thick Pd/Ag foil. To date, the inability of the thin Pd/Ag coatings to transport hydrogen is attributed to the following factors in order of decreasing severity: (1) carbon due to insufficient burn-out, (2) oxidation during sintering, (3) low Pd content in the ink: 75%-77% Pd is desirable, and (4) contamination from support elements such as Fe and Cr.

It may be argued that the leak-tight nature of the Pd/Ag coatings is an artifact of the carbon deposition in the coating. If this were the case, all of the coated samples (25 polished and unpolished samples were coated using the direct-write process) would be expected to display leak-tight behavior. The fact that leak-tight behavior was noticed only with the polished samples supports the theory that the leak-tight behavior was not due to plugging of the porous substrates by coking or carbon deposition.

## **2.2. Technical Approach**

The four major tasks outlined in Section 2.0 will be addressed as follows:

### **2.2.1. Task 1. Hydrogen Permeation Through Thin Membranes**

The following tasks will be performed to yield a thin leak-tight Pd/Ag coating that transports hydrogen.

*Optimization of Pd/Ag Ink*

Collaborations with MRA to minimize the organic content of the Pd/Ag ink will be conducted. MRA currently supplies inks for use in the electronics industry. These inks are too viscous (33,000 cPs at 25 °C) for Pd/Ag coating service. The required viscosity of the Pd/Ag ink will be established to meet the needs of the laser direct-write process (PPI), and in the process, heavy organics such as ethyl hydroxyl-ethylcellulose will be minimized or eliminated.

The organic burn-out protocol will be established using thermal gravimetric analysis (TGA) at MRA. TGA of a 30Pd/70Ag ink (inks rich in silver are commonly used in the electronics industry) was conducted recently (in air) and revealed the following: organic burnout: 350 to 375 °C; Palladium oxide formation: 400 to 700 °C; and PdO decomposition to Pd at temperatures greater than 700 °C. Increasing the Pd content to 75-77% would shift the oxidation window to a higher temperature. The temperature and soak time for complete burn-out of organics will be identified based on TGA of a 75%-77% Pd ink. Note that during Phase I, the samples were not subjected to a burn-out step fearing oxidation of the coating; after coating, the samples were "soft-baked" at 150 °C to drive-off volatile matter and were then sintered in nitrogen at 850 °C to 900 °C. This procedure led to carbon formation as confirmed by electron probe microanalysis.

During the Phase I period, a 70Pd/30Ag composition was utilized since it was readily available. MRA has agreed to supply us with a Pd-Ag formulation that contains 75-77%Pd, which exhibits a maximum in hydrogen permeability for Pd-Ag alloys [2-4].

*Deliverable:* (1) Report identifying optimum Pd/Ag ink formulation, and (2) Protocol for burn-out of organics from the 75%-77% Pd/Ag ink that shows complete organic burnout without Pd/Ag oxidation or carbon deposition.

*Optimization of Porous Metal Substrates Pre-Treatment*

Polishing of the porous metal substrates using pulsed ion beam treatment (done at QMT) results in a leak-tight coating. Polishing is accompanied by some reduction in surface porosity. The ion-beam strength and exposure time can be varied to achieve polishing without affecting surface porosity.

Other high temperature alloy porous metals such as Inconel or Hastelloy which are more resistant to sintering could be used. Hastelloy X and Inconel 600 porous



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metal substrates may be . These alloys are also amenable to surface polishing by ion beam treatment.

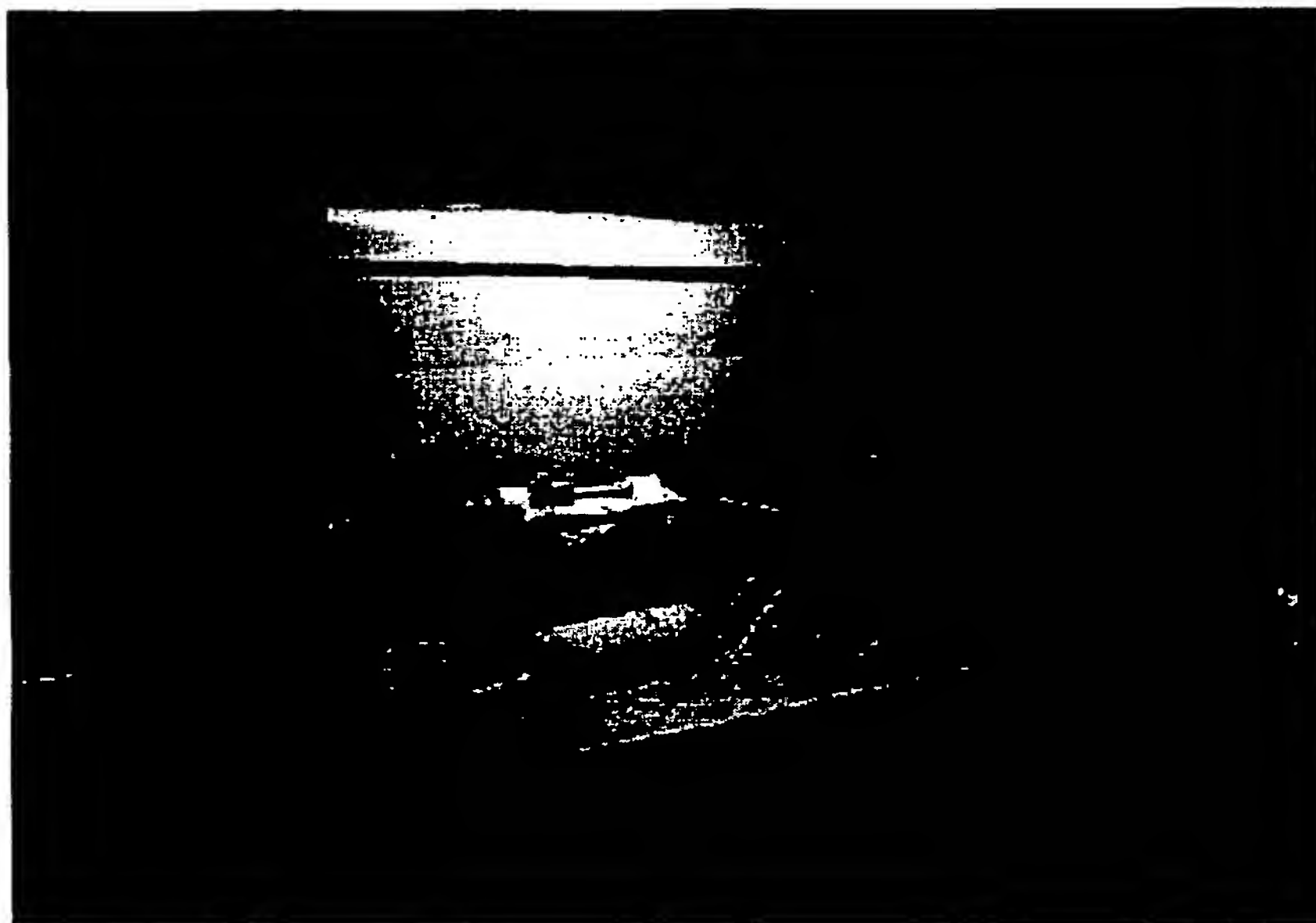
As mentioned in Section 2.1, some evidence of intermetallic diffusion was found between the support material and Pd/Ag coating. Alternate diffusion barrier strategies such as sputtering a fine layer of titanium nitride or tungsten [12, 13] on the porous metals prior to Pd/Ag deposition may be used. A deposited porous ceramic layer may also be used, but due to expected adherence problems between the metal support and the ceramic layer, especially commensurate with any temperature cycling, may not be optimal yet still usable.

#### *Pd/Ag coatings*

Leak-tight Pd/Ag thin membrane deposition using the Laser Direct-Write Process has been demonstrated. A leak-tight coating after 3-coating cycles (coating/soft bake/sintering), optimization of the coating parameters and ink composition may permit a leak-tight coating using a single cycle has been obtained. EPMA analysis showed the presence of oxygen and carbon throughout the thickness of the coating. While the carbon content can be managed by optimizing the ink composition and burn-out, the sintering protocol needs to be addressed to eliminate oxidation. The choice of the soak temperature was a compromise between the need for adequate sintering of the Pd/Ag film without over-densification of the stainless steel support (support densification is a function of the number of coating cycles, maximum temperature during sintering protocol and the support itself). It was also desired to maintain a high enough soak temperature that would alleviate concerns of Pd oxidation (via decomposition of PdO). Ramp rates were based on rates that were being used for another material (that was sensitive to thermal shock and expansion mismatch). Faster ramp rates may prove to be more appropriate for the Pd/Ag coating since the oxidation window (expected to be 400 to 750 °C for 75% Pd) would be crossed more rapidly. Longer soak times and/or higher soak temperature may also prove to be beneficial. The sintering protocol will be assessed using TGA. After burn-out of the organics, sintering in a lean hydrogen stream (instead of nitrogen) above 400 °C is contemplated to mitigate oxidation, and will also be evaluated.

### **2.2.2. Task 2. Demonstrate Hydrogen Permeation, Lifetime and Stability to Thermal Cycling**

Substrates containing a leak-tight Pd/Ag coating, as identified in Task 1, are to be subjected to hydrogen permeation tests. Once demonstrated hydrogen permeation at high purity levels through our Pd/Ag coated substrates (composite membranes) is shown, the next step would be to subject these membranes to long-term stability tests (at least 250 h) and stability to thermal cycling (at least 10 cycles from cold to 600 °C). These tests conducted using a 75% $H_2$ /25% $N_2$  feed and performed in our hydrogen permeation apparatus (Figure 1.6).



**Figure 1.6. Hydrogen Permeation Test Bench.**

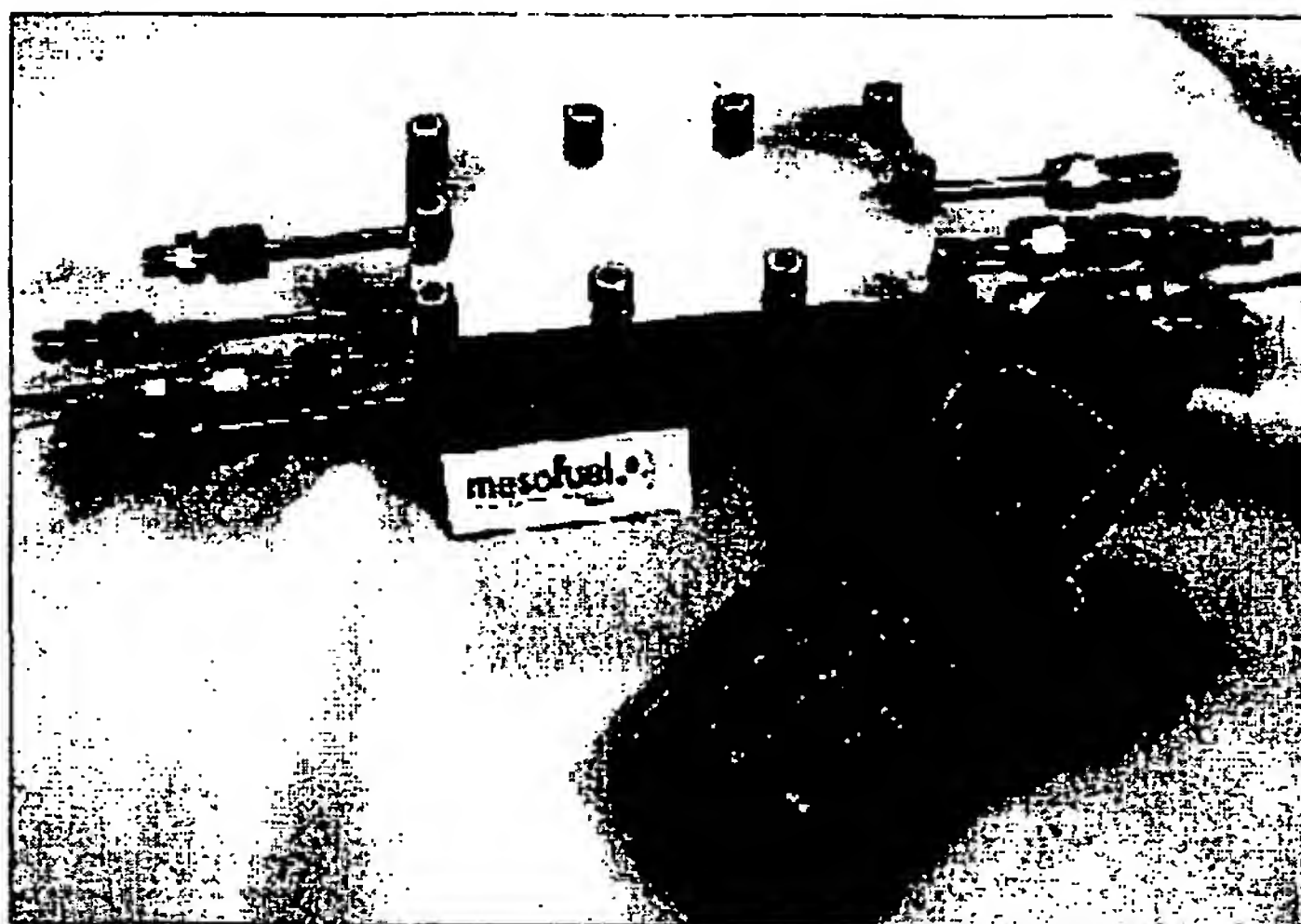
Hydrogen permeation and purity will be monitored as a function of time. Possible failure modes may include contamination of the Pd/Ag coating by intermetallic diffusion from the support that would result in decreasing hydrogen permeation (life time tests) and/or peeling-off or flaking of the coating during the thermal cycling tests. Problems arising from intermetallic diffusion can be solved by a proper choice of diffusion barrier, porous support and treatment protocols during the coating process. As discussed in Section 2.1, minimal diffusion of the stainless steel constituents such as Fe and Cr into the Pd/Ag coating was observed, while employing an oxide diffusion barrier. During permeation tests, hydrogen permeating through the coating may gradually destroy the chromium oxide barrier. Consequently, other candidates for

EV 311270660 US

diffusion barriers are to be evaluated under Task 1. No flaking or cracking of the coated samples that underwent between 3 to 7 cycles between room temperature and 900 °C was observed, and no anticipated major roadblocks based on this issue expected.

### **2.2.3. Task 3. Scale-up of Hydrogen Separation Membranes and Integration into our MesoChannel Membrane Reformer**

A coating a 7cm x 4 cm x 1 cm porous metal substrate (length x width x thickness) should be straightforward. Substrates of these dimensions can be cut using water-jet from larger sheets. Currently, such sized SS316 porous substrates are utilized as a support for the Pd-Ag foil in our membrane reformers. Inconel substrates have also been evaluate. A photograph of a MesoChannel Membrane reformer is shown in Figure 1.7 below.



**Figure 1.7.** Photograph of a MesoChannel First Generation membrane reformer.

Pure hydrogen production from a wide range of hydrocarbons using this membrane reformer (integrated hydrogen separation membrane-reformer-combustor) design, and have also demonstrated powering a PEM fuel cell using the hydrogen that was produced from it (*details in Section 1.2 of our Phase I report*). Currently, the 25 micron thick Pd/Ag foil is sealed using Grafoil gaskets. The porous metal substrate will contain a non-porous metal frame that can be easily welded or brazed into the



EV 311270660 US

reformer body. Therefore in addition to improving the performance of the reformer (via higher hydrogen permeation rates), the substrate-coated composite membrane should allow for ease of integration resulting in reduced weight (removal of flanges, screws, gaskets shown in Figure 1.8), and reduced leakage around the gaskets.



**Figure 1.8.** Solid model of the reformer which would house the thin Pd/Ag membrane coated on porous metal supports (note the absence of flanges seen in Fig. 1.7 above).

Therefore, integration of such a composite membrane is a revolutionary step for efforts to generate pure hydrogen for PEM fuel cell applications.

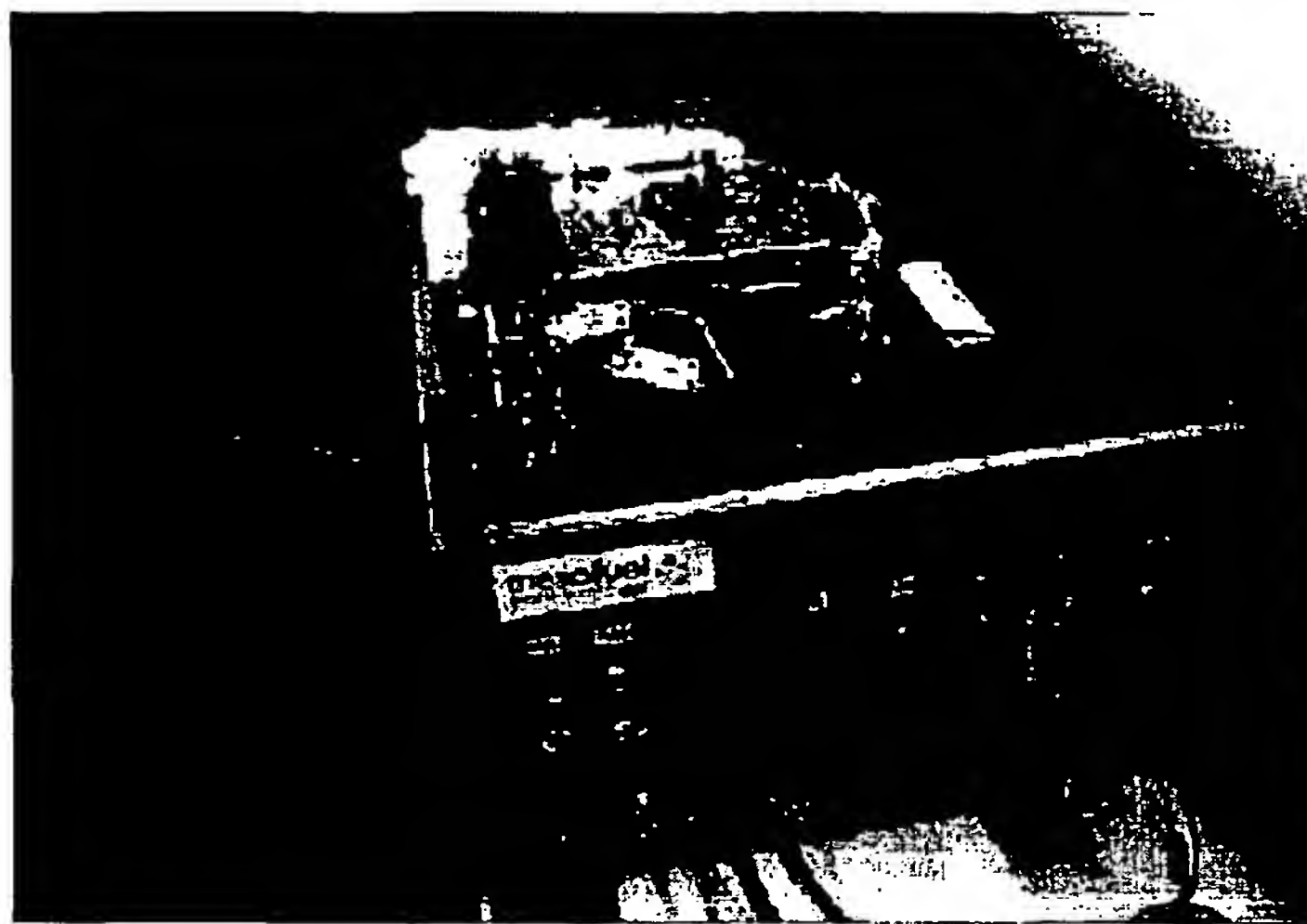
#### **2.2.4. Task 4. Pure Hydrogen Production from Light Hydrocarbons using Composite Thin Membranes in our MesoChannel Membrane Reformer**

Pure hydrogen production from a wide range of hydrocarbons ( $C_1$ - $C_{12}$ ) using our membrane reformer has been demonstrated. The membrane reformer comprises of an integrated reformer, combustor and hydrogen separation membrane that permits pure hydrogen production in a single unit. Optimum catalyst formulations for both reforming and combustion services have been identified and have accumulated a cumulative testing time of over 1000 h for the catalysts. Analytical protocols and the necessary equipment to conduct reforming tests have been established. Currently, two gas chromatographs (Shimadzu, GC-1 7A) that are equipped with flame ionization

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detectors and thermal conductivity detector and methanizer for both permanent gas and hydrocarbon analysis are available and will be utilized.

In addition to hydrocarbon reforming, pure hydrogen production from ammonia decomposition in our membrane reformers has been demonstrated. A photograph of a packaged unit is shown in Figure 1.9 to demonstrate a move of hydrogen generators from the lab-bench to field testing and for utilization in PEM fuel cell power systems<sup>3</sup>.



**Figure 1.9.** Photograph of MFI's Ammonia-Based Pure Hydrogen Generator Prototype that is ready for field testing. In the background is MFI's Membrane Reformer; in the foreground is a 50W PEM FC.

The package contains essential balance-of-plant components (valves, pumps etc.) and a control board to run the unit at a constant hydrogen output of 1.5 SLPM (sufficient for 100 W power production using a PEM fuel cell). A hydrocarbon reforming unit, which will also be subjected to field testing, is currently being packaged. In these prototypes, the hydrogen separation membrane is a commercially available 25 micron thick 75Pd/25Ag foil. As mentioned previously, a high performance thin composite Pd-Ag membrane into our membrane reformers is integration of anticipated.

Reformation of light hydrocarbons (methane, propane) in membrane reformers that contains the Pd/Ag coated porous substrate at conditions similar to previous tests using a reformer that contained a Pd/Ag foil (*Section 1.2, Phase I report*) will be conducted. Hydrogen production will be evaluated as a function of temperature,

EV 311270660 US

pressure and space velocity, and improvement in performance relative to the commercial Pd/Ag foil will be assessed.

Packaging of the MesoChannel Reformer into a compact pure hydrogen generator, and field testing will be performed.

## References

1. T. L. Ward and T. Dao, "Model of hydrogen permeation behavior in palladium membranes", J. Mem. Sci. 153, 211-231 (1999).
2. G.J. Grashoff, C.E. Pilkington and C.W. Corti, "The purification of hydrogen", Plat. Met. Rev. 27(4), 157-169 (1983).
3. A.G. Knapton, "Palladium alloys for hydrogen diffusion membranes", Plat. Met. Rev. 21,44-50 (1977).
4. G. Holleck, "Diffusion and solubility of hydrogen in palladium and palladium-silver alloys", J. Phys. Chem. 74(5), 503-511 (1970).
5. T.C. Pluym, SW. Lyons, Q.H. Powell, A.S. Gurav, T.T. Kodas, L.M. Wang and H.D. Glicksman, "Palladium metal and palladium oxide particle production by spray pyrolysis", Mat. Res. Bull. 28, 369-376 (1993).
6. K. Nagashima, T. Himeda, and A. Kato, "Properties of conductive films made from fine spherical silver-palladium alloy particles", J. Mater. Sci. 26, 2477-2482 (1991).
7. K. Nagashima, M. Wada, and A. Kato, "Preparation of fine Ni particles by the spray pyrolysis technique and their film forming properties in the thick film method", J. Mater. Res. 5(12), 2828-2834 (1990).
8. Shu, B.P.A. Grandjean, A. Van Neste, S. Kaliaguine, "Catalytic palladium-based membrane reactors: a review, Can. J. Chem. Eng. 69, 1036-1060 (1991).
9. S.S. Cole, Jr. "Oxidation and reduction of palladium in the presence of silver", J. Am. Ceram. Soc. 68 (4), C106-C107 (1985).
10. S F. Wang and W. Huebner, "Thermodynamic modeling of equilibrium subsolidus phase relation in the Ag-Pd-O<sub>2</sub> system", J. Amer. Ceram. Soc. 74(6), 1349-1353 (1991).

EV 311270660 US

11. P. Mardilovich, Y. H. Ma and Y. She, "Hydrogen gas-extraction module and method of fabrication", US Patent 6152987.
12. J. Shu, A. Adnot, B.P.A. Grandjean, S. Kaliaguine, "Structurally stable composite Pd-Ag alloy membranes: Introduction of a diffusion barrier", Thin Solid Films, 286, 72-79 (1996).
13. V.M. Gryaznov, O.S. Serebryannikova, Yu.M. Serov, "Preparation and catalysis over Pd composite membranes" Appl. Catal. A: General, 96, 15-23, 1993.



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INVENTOR(S)					
Given Name (first and middle [if any])	Family Name or Surname		Residence (City and either State or Foreign Country)		
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TOM	VENCILL		Albuquerque, New Mexico		
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<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
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<input checked="" type="checkbox"/> Specification		Number of Pages	<u>23</u>	<input type="checkbox"/> CD(s), Number	
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<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,

SIGNATURE

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